Small-Angle Light Scattering of Phase Separation Structures in Polymer Blends

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Small-angle light scattering of phase separation structures in polymer blends

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The correlation function presented by Debye *et al.* for characterizing the random two-phase structure in solids is further extended by considering an effect of partial ordering to describe the statistical features in phase separation structures of polymer blends. The new correlation function is in the form $\gamma(r) = \exp(-r/a_0)\cos(q_0 r)$ with two parameters. The scattering intensity distribution calculated from this function can predict a maximum whose sharpness and position are characterized by a_0 and q_0. Good agreement was achieved between the calculated intensity and measured small-angle light scattering curve from phase-separated poly(methyl methacrylate)/poly(vinyl acetate) blends.

I. INTRODUCTION

In general, the phase separation structures of polymer blends have poor regularity in shape and size. The small-angle light scattering (SALS) is a useful technique for quantifying the heterogeneities of dimension comparable to the wavelength of the incident light.[1] The most prominent feature of the SALS pattern for the isotropic heterogeneous systems is the occurrence of a scattering ring.[2,3] This phenomenon can be observed in most cases where the phase separation structure is formed by spinodal decomposition[4–8]. By this mechanism the concentration fluctuations grow larger with time after quenching the mixture into the miscibility gap and bring about a high interconnectivity in phase structures. At the same time the light is scattered due to the concentration fluctuations to form a scattering ring which increases in intensity and moves towards the main beam with time. The growth dynamics of concentration fluctuations in the early stage of spinodal decomposition of polymer blend systems have been studied by many researchers,[6–14] based on the Cahn–Hilliard–Cook theory.[15,16] However, few investigations are concerned with the characterization of the single broad peak as found in SALS experiments of polymer blend systems.

The phase separation structures formed in amorphous polymer blends can be characterized as: (1) dense packing, (2) low regularity in shape and size but with partial ordering in structures, which may be originated from average size of domains, rather than completely random arrangement, and (3) the dimensions on the order of 10^0–10^2 micrometers. These make SALS a powerful means to investigate the statistical features in phase separation structure.

Theoretical studies of the light scattering from solid materials were first carried out by Debye and Bueche (DB)[17] for isotropic inhomogeneous systems. This was extended to systems containing fluctuations in anisotropy by Goldstein-Michalik,[18] and further to crystalline polymers by Stein and his co-workers.[19–21] Debye *et al.*[22] have shown that a correlation function with exponential type is theoretically expected for a randomly arranged two-phase system with sharp boundaries. The correlation function technique was used for the study of polymer blends by Moritani *et al.*[23] in terms of summation of short- and long-range fluctuations. Yuen and Kinsinger[24] fitted their data, in a similar way, to a combination of two exponential-type correlation functions.

We present here a correlation function by considering an effect of partial ordering in structures from a phenomenological point of view. Using this correlation function an intensity distribution, which predicts an appearance of maximum, can be obtained to characterize the scattering of isotropic phase separation structures based on DB theory. Comparison with experiments shows that good agreement between experimental and calculated intensity profiles can be achieved. We have also noted that a number of models[25–27] have been proposed recently to interpret the scattering peak observed in microemulsion systems by small-angle scattering. Due to the similarity in scattering patterns between the polymer blend and the microemulsion systems, our treatment may provide some statistical explanations to the structures formed in microemulsions.

II. THEORY

A. Background

According to the DB theory,[17] the intensity of scattered light can be expressed in terms of the correlation function

$$I(\mathbf{q}) \sim \int \gamma(\mathbf{r}) \exp(-i\mathbf{q}\cdot\mathbf{r})\, d\mathbf{r}, \tag{1}$$

here $\mathbf{q}$ is the scattering vector, its magnitude is equal to $(4\pi/\lambda)\sin(\theta/2)$ with wavelength λ, and scattering angle θ. The correlation function is defined as

$$\gamma(\mathbf{r}) = \int \eta(\mathbf{r}+\mathbf{r}')\eta(\mathbf{r}')\, d\mathbf{r}' \Big/ \int \eta^2(\mathbf{r}')\, d\mathbf{r}', \tag{2}$$

where η is the fluctuation of the local polarizability from its average value. Equation (2) describes the spatial extent of the fluctuation. For spherically symmetrical systems, Eq. (1) can be written as

$$I(q) = \langle \eta^2 \rangle \int_0^\infty \gamma(r) \frac{\sin(qr)}{qr} 4\pi r^2\, dr. \tag{3}$$

$\gamma(r)$ and $\langle \eta^2 \rangle$ may be determined from Fourier inversion of the scattered intensity by

$$\gamma(r) = \int_0^\infty I(q) \frac{\sin(qr)}{qr} q^2 dq \Big/ \int_0^\infty I(q) q^2\, dq,$$

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$$\langle \eta^2 \rangle = \int_0^\infty I(q) 4\pi q^2 \, dq \, .$$

In the case of a distribution of scatterers with random shape and size in a solid, Debye *et al.*[22] have shown that the scattering can be characterized by an exponential correlation function

$$\gamma(r) = \exp(-r/a_0), \tag{4}$$

where a_0 is called a correlation distance. Upon substituting Eq. (4) into Eq. (3), integration gives

$$I(q) = 8\pi \langle \eta^2 \rangle a_0^3/(1 + a_0^2 q^2)^2. \tag{5}$$

Equation (5) shows a monotonic decrease in scattered intensity and a q^{-4} decay at large q.

Correlation distance L_c can be determined in terms of correlation function by

$$L_c \equiv \int_0^\infty \gamma(r) dr = a_0. \tag{6}$$

The first equality of Eq. (6) always holds, regardless of whether or not an exponential function is used.

B. A new correlation function

The existence of the maximum in a scattering profile is inconsistent with the models as shown above and imply that a degree of periodicity exists within limited distance from any point in these structures. This can be brought about by a partial ordering of particles or rod-like domains, or by occurrence of highly interconnected structures. These characteristics must be reflected in the form of a correlation function. As shown by Teubner and Strey,[26] a kind of periodic function seems to be needed in the correlation function to produce this maximum. We adopted here a cosine function and retained the exponential function in Eq. (4) to define a new correlation function in the form

$$\gamma(r) = \exp(-r/a_0)\cos(q_0 r), \tag{7}$$

where q_0 is a new parameter introduced with a dimension of [1/length] whose physical meaning will be discussed later. The general shape of Eq. (7) is shown in Fig. 1 and compared with that of Eq. (4). The periodic damping function given by Eq. (7) is characterized by two parameters, a_0 and q_0. Parameter a_0 affects the decay rate of the correlation function with increasing distance r, and may be considered as a measure of macroscopic nature of the structure; while parameter q_0 determines the periodicity of the correlation function, and gives the local information on average size of domains. Unlike the simple exponential correlation function Eq. (4), negative regions appear in Eq. (7). This can be understood by considering that the existing probabilities of scatterers in these distances are very low, or in other words, the space possessed by a certain scatterer cannot be occupied by another one. This is similar to the excluded volume of a particle system with certain particle dimensions. The distances between the centers of scatterer may be expected to be on the order of $1/q_0$. Furthermore, the new correlation function satisfies the following boundary conditions: $\gamma(0) = 1$; $\gamma(\infty) = 0$.

The scattering intensity can be determined by using Eqs. (3) and (7)

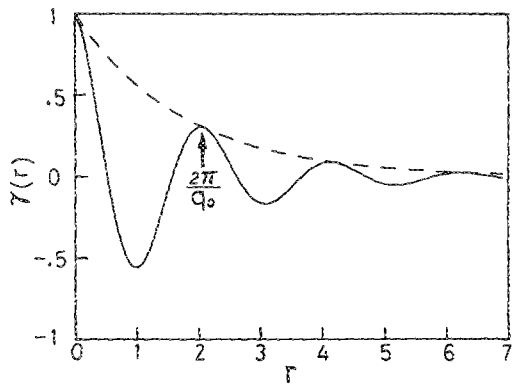

FIG. 1. Comparison between Eq. (7) (solid line) and exponential (dashed line) correlation function.

$$I(q) = 4\pi \langle \eta^2 \rangle a_0^3 \times \left\{ \frac{1 + q_0/q}{[1 + a_0^2 (q + q_0)^2]^2} + \frac{1 - q_0/q}{[1 + a_0^2 (q - q_0)^2]^2} \right\}. \tag{8}$$

In contrast to Eq. (5), Eq. (8) is made up of two terms which differ with each other only in the sign in front of parameter q_0. Figure 2 shows the variation of intensity with wave vector q by solid line. The functional form of Eq. (8) yields a single broad maximum which is confirmed by experiment. The q_0 influences the position of the maximum, and a_0 the sharpness of the curve. Therefore, the physical meaning of parameter a_0 and q_0 may be viewed in such a way that the a_0 expresses a degree of partial ordering in structures; while the q_0 expresses a measure of periodicity existing in the domains. Also a characteristic q^{-4} dependence of intensity distribution at large wave vector q is predicted from Eq. (8).

The correlation distance corresponding to Eq. (7) is given by

$$L_c = a_0/(1 + a_0^2 q_0^2). \tag{9}$$

It can be shown that the Debye's random two-phase model is a special case of the model we mentioned here. In fact, Eqs. (4), (5),and (6) can be obtained from Eqs. (7), (8),and (9), respectively, by putting $q_0 = 0$.

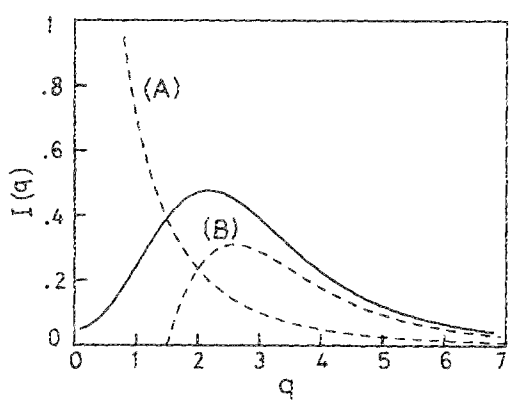

FIG. 2. Intensity distribution given by Eq. (8), solid line. Dashed lines (A) and (B) show the contribution of the first and second terms.

III. COMPARISON WITH SCATTERING EXPERIMENTS

A. Experimental

Blends of poly(methyl methacrylate)(PMMA) and poly(vinyl acetate)(PVAc) were used in the investigations of the phase separation behavior. Polymer specimens were commercial ones supplied by Wako Pure Chemical Industries Ltd. The PMMA had a weight-average molecular weight of $Mw = 9.8 \times 10^4$ and a molecular weight distribution index of $Mw/Mn = 1.9$; while the PVAc had $Mw = 2.1 \times 10^5$ and $Mw/Mn = 3.0$. PMMA and PVAc were dissolved at 10 wt% of total polymer in a common solvent chloroform. The solution was casted onto a slide glass at room temperature. The chloroform was evaporated at the natural rate, and a thin solid film, with thickness of 100–150 μm, was obtained after about 5 min. The solvent-cast films were further dried in a vacuum oven at 40 °C for more than three days.

The isothermal phase separation behavior was studied by using SALS equipped with a programmable heating chamber. The light source was a He–Ne gas laser with a wavelength of 632.8 nm and a power of 5 mW. The blend film on the slide glass was inserted into the heating chamber kept at a constant temperature. Intensity of light scattered was detected as voltages by photodiode. Data treatment such as background subtraction, sensitivity correction, signal smoothing, and averaging was performed by an off-line computer.

The solution-cast films of PMMA/PVAc blend were transparent in all compositions and did not show any gross phase separation as viewed by optical microscope. After a temperature jump to above 130 °C, an interconnected domain structure was observed, followed by an increase in size with time. Figure 3 shows a typical SALS pattern. The single circular halo decreased in angle and increased in intensity as the phase separation process progressed.

B. Application

A series of time development of measured intensity curves at constant temperature was used to compare with the theoretical intensity distributions [Eq. (8)]. Figure 4

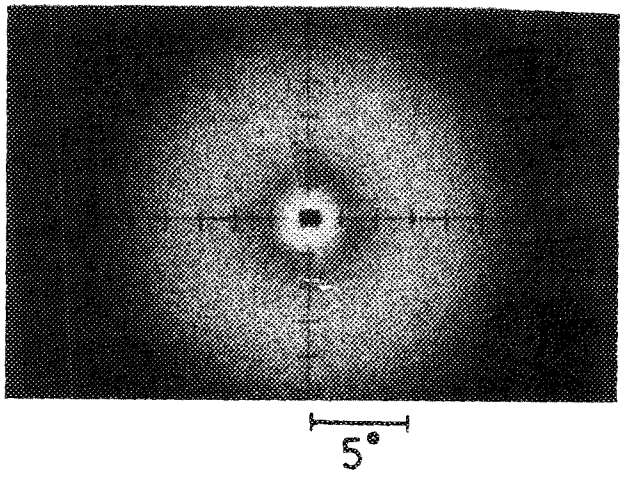

FIG. 3. Photograph of SALS pattern obtained from PMMA/PVAc (30/70) blend.

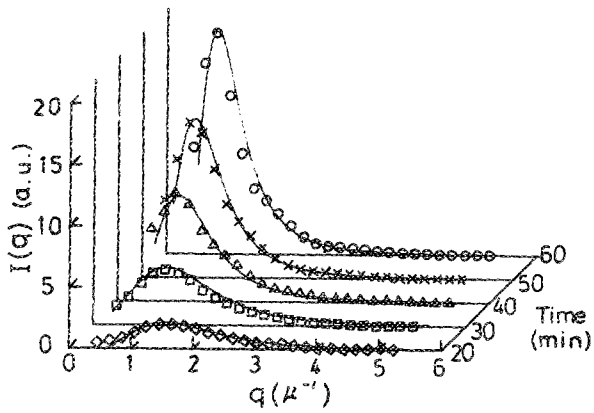

FIG. 4. Scattering intensity distributions of PMMA/PVAc (30/70) blend for 164 °C at various times. Solid lines were determined by Eq. (8) with parameters in Table I.

shows the SALS profiles at 164 °C for the system PMMA/PVAc weight ratio (30/70). Using a nonlinear least-squares method, we determined the characteristic parameters a_0 and q_0 by fitting the scattering data. As can be seen the shape of $I(q)$ profile is almost perfectly reproduced using the two parameters. There is a trend in Fig. 4 that scattering curves change to lower q value and become sharper with time; this corresponds to decreasing values of q_0 and increasing values of a_0 (Table I).

The experimental results shown in Fig. 4 are considered in the intermediate and late stages of phase separation because the position scattering maximum changed with time. Furthermore, the intensity and position of the maximum are expressed by the power law for the late stage. The details on the dynamics of this system will be discussed elsewhere.[28] In the early stage where the linearized Cahn–Hilliard theory is applicable, Eq. (8) may also be available. However, the early stage was too short to observe in this system. Consequently, we could not examine the applicability of Eq. (8) at the early stage.

A typical form of the new correlation function is presented in Fig. 5(a) using the parameters obtained from a PMMA/PVAc (30/70) mixture at 164 °C and 40 min. Deviation between the new correlation function and the exponential function (dashed line) can be seen in the region of distance $r = 2$ μm. This difference is enlarged in Fig. 5(b). The negative region corresponds to a poorly existing probability of scatterers, implying a preservation of short range order. The position of minimum may be able to give the statistical average size of domains. The value of correlation

TABLE I. Variation of fitted characteristic parameters a_0,q_0 and corresponding correlation distance L_c with time for the measured scattering curves of PMMA/PVAc (30/70) blend at 164 °C.

Time/min	a_0/μ	q_0/μ^{-1}	L_c/μ
20	0.63	1.05	0.44
30	0.71	0.80	0.54
40	1.00	0.66	0.70
50	1.18	0.57	0.81
60	1.34	0.55	0.87

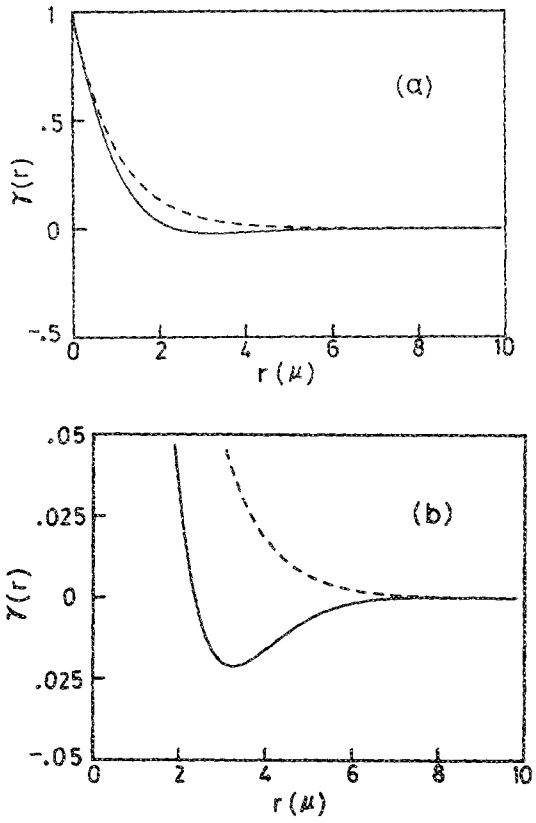

FIG. 5. (a) Comparison between Eq. (7) (solid line) and exponential (dashed line) correlation functions for PMMA/PVAc (30/70) blend, 164 °C, at 40 min using parameters in Table I. (b) Enlargement of (a) for small $\gamma(r)$.

function approached zero rapidly with increasing r, indicating that the distortions in structures lead to a loss of long range order.

We noted some deviations appeared at low q in Fig. 4. These can be attributed partially to the influence from the beam stopper, which made it difficult to detect the true intensity at the wave numbers close to $q = 0$. Another possibility is due to an inadequacy of Eq. (8),which tends to give a negative value at low q in some cases as shown in Fig. 4. The value of q_0 is not numerically equal to that of $q_{\max}$ at which the intensity distribution gives a maximum. It is obvious from Eq. (8) and Fig. 2 that position of maximum is affected mainly by parameter q_0, and also partially by parameter a_0. In the cases studied here, values of q_0 are smaller than that of $q_{\max}$.

A very similar pattern of small-angle scattering was also observed in the microemulsion systems with bicontinuous structures.[25–27] Berk[25] gave a mathematic approach based on the Cahn's theory of spinodal decomposition and predicted qualitatively the appearance of a scattering peak. Teubner and Strey[26] obtained an intensity distribution in form of $I(q) \sim (a_2 + c_1 q^2 + c_2 q^4)^{-1}$ using an order parameter expansion of the Landau free energy function. This distribution yields a single broad scattering peak for $a_2 > 0$, $c_1 < 0$, and $c_2 > 0$, and leads to a correlation function with a similar form to Eq. (7). In their model, three parameters have to be determined by fitting. Another model, with two parameters, was presented by Vonk *et al.*[27] based on a disordered lamellar structure. They were able to fit a variety of scattering curves well. However, a distribution function of lamellae thickness (they adopted a gamma function) had to be introduced to characterize the maximum in intensity scattered at zero scattering vector and an additional parameter was needed. It can be shown for this case that Eq. (8) changes continuously from an expression which exhibits a maximum to the Debye's expression Eq. (5) in the limit of $q_0 = 0$.

IV. CONCLUSIONS

We have proposed a new correlation function, with the form of $\gamma(r) = \exp(-r/a_0)\cos(q_0 r)$, to describe the statistical features of isotropic phase separation structures in polymer blends by considering the effect of partial ordering. The corresponding intensity formula predicts a single broad peak as observed in SALS experiments. Parameters a_0 and q_0 can be partially separated to characterize the sharpness of distribution and position of maximum, respectively. By putting $q_0 = 0$, the results reduce to the model of completely random two-phase structure described by Debye *et al.* The intensity distribution derived from the new correlation function satisfactorily describes the scattering curves of phase-separated PMMA/PVAc systems.

ACKNOWLEDGMENTS

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